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It was the purpose of this study to investigate the thermal analysis of the first transition metal series of oxalates ($MC_2O_4 \cdot XH_2O$, M = Cr, Mn, Fe, Co, Ni, Cu, Zn) and squarates ($MC_4O_4 \cdot XH_2O$, M = Cr, Mn, Fe, Co, Ni, Cu, Zn). It was hypothesized that there would be no difference in the end product between the decomposition of oxalate and squarate compounds. It was also hypothesized that there would be some similarities between oxalates and squarates in terms of bonding structure as well as the relationship of bond strength and size of metal radii.

The attempted synthesis of the fourteen oxocarbon anion salts was successful. The synthesis of $CuC_2O_4 \cdot XH_2O$ under N_2 atmosphere was also included.

The activation energy and order of reaction of each compound was computed. Three generally accepted kinetic models are used: A. W. Coates and J. P. Redfern, E. S. Freeman and B. Carroll, and Walter K. Tang.

This is an initial report of the kinetic parameters for the first transition series of metal squarates.

A STUDY OF THE THERMAL DEHYDRATION AND DECOMPOSITION OF OXOCARBON ANION SALTS OF TRANSITION METALS

by

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APPROVAL PAGE

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INTRODUCTION

Oxocarbon Anion Salts of Transition Metals - The thermal dehydration and decomposition of a series of transition metal oxalates ($MC_2O_4 \cdot XH_2O$, M = Cr, Mn, Fe, Co, Ni, Cu, and Zn) and squarates ($MC_4O_4 \cdot XH_2O$, M = Cr, Mn, Fe, Co, Ni, Cu, and Zn) have been investigated using vacuum thermal gravimetric analysis (TG) and differential thermal analysis (DTG) under helium. An interpretation of kinetic parameters of thermal dehydration and decomposition as well as other factors influencing the mode of dehydration and decomposition will be given in this study.

Thermal Dehydration and Decomposition of Metal Oxalates - Early Work - Although the thermal dehydration and decomposition of metal oxalates have been widely investigated, the parameters reported by each researcher for an individual oxalate were frequently different.

For instance, as early as 1954 Ya. A. Ugai[1] published thermograms whose results showed that metals were the end products in a number of cases of thermal decomposition of metal oxalates. In his study, Ugai dealt primarily with the decomposition of the oxalates of the bivalent metals Ni, Co,

Fe, Mn, Zn, Cd, Mg, Pb, Sn, Ca, Sr, Ba, Hg, Cu, and dihydrate of oxalic acid. Ugai's experiments resulted in the establishment of endothermic and exothermic types of heating curves for the thermal decomposition of bivalent metal oxalates; the strongly exothermic nature of the decomposition of copper and mercury oxalates; the fact that "superheating" is present in both the dehydration process and during decomposition of the anhydrous salts and that oxalates without water crystallization give a well-defined "superheat" cycle; the irreversible transformation of the unstable form of a solid into the thermodynamically stable crystalline form of a solid; and the fact that the form of thermograms depends on the character of individual oxalate decomposition. Thus, through thermographic analysis, Ugai proved that metals were end products of thermal decomposition of metal oxalates for Ni, Co, and Fe, while Mn, Zn, Mg, Pb, and Sn produced metal oxides.

V. P. Kornienko[2] in 1957 advanced a step further in methodology when he suggested that by heating the oxalates isothermally in sealed-evacuated containers one could produce as end products mixtures of metals and their oxides.

In a broad study of thermal decomposition of oxalates, D. Dollimore[3] and his associates over a period of time were able to determine that the variation of the surface area of

oxalates was in direct relation to the temperatures of treatment in air. Part I of Dollimore's study attempted to determine if Gregg's method[4] for the production of a greater number of product particles from a given number of reactant particles could be extended to more complicated decomposition processes taking place on the thermal treatment of oxalates in air. The result was that, in general, the lower the temperature of decomposition, the greater the increase of surface area.

Building on the studies of Ugai and Kornienko, Dollimore attempted in the second part of his study[5] to examine "the thermogravimetric analysis of these oxalates in air and in nitrogen, and suggestions are made as to the manner of their decomposition." Dollimore was able to prove thermogravimetrically that, in some cases, oxalate decomposition proceeds directly to the oxide but that in some cases metal is first formed and then subsequently oxidised in air to the oxide. Generally, Dollimore found that decomposition occurring in nitrogen is simpler than that occurring in air and that decomposition in nitrogen produces either the metal or a lower oxide.

Later studies conducted as parts of Dollimore's extensive study of thermal decomposition of oxalates dealt exclusively with the decomposition and surface properties of zinc oxalate dihydrate, nickel oxalate dihydrate, and cobalt oxalate

dihydrate. In these studies[6] Dollimore discussed in great detail the correlation of changes in surface area with the kinetics of thermal decomposition. The end result of Dollimore's in-depth study was proof that when the anhydrous salt is rehydrated and then decomposed, a porous zinc oxalate is obtained with a surface area much larger than that of the non-porous material.

Two years after Dollimore's study, E. D. Macklen[7] studied the thermal decomposition of manganese, cobalt, and nickel oxalate dihydrates. Using TG and DTG in air and nitrogen atmospheres, Macklen determined that in nitrogen the decomposition of oxalates yields the metal oxide, MO, first. In the case of cobalt and nickel, MO is then reduced to metal by "nascent" carbon monoxide. Macklen also obtained correlations between inert atmosphere decomposition temperatures and cation electronegativities. Macklen's study determined that in air, the initial decomposition temperature is lower than in nitrogen due to the oxidation of the cation from the divalent to the trivalent state and that a correlation between the case of oxidation and temperature reduction did exist.

In examining the thermal decomposition of Mg, Mn, Fe, Co, and Zn oxalates, Lagier and his co-workers[8] determined that the phases of decomposition observed depended on the method of preparation.

However, it was K. Nagase[9] of Japan who went beyond Dollimore and Macklen's findings in his study of the thermal dehydration and decomposition of the bivalent metal oxalates in a solid state. Nagase went on to discuss the relation between the nature of the metal ions and the initial weight-loss temperature or enthalpy changes. After much experimentation, Nagase claimed that the decomposition of the metal oxalates to the metal oxides may be initiated by M-O (ox) bond breaking, since these oxalates decomposed at higher temperatures as 1/r increased (where r denotes the radius of the metal ion). On the other hand, the oxalates of Co, Ni, and Cu, which decompose at lower temperatures as 1/r increases, may be decomposed by electron transfer from the oxalate ion to the metal ions.

According to Nagase, the thermal analysis of metal oxalates can be considered in two steps: first, the dehydration in which the water molecules are eliminated from the metal oxalates,

$$MC_2O_4 \cdot 2H_2O \rightarrow MC_2O_4 + 2H_2O \qquad (1)$$

and secondly, the decomposition of the metal oxalates which may be expressed by

$$MC_2O_4 \rightarrow MO + CO + CO_2 \qquad (2)$$

or

$$MC_2O_4 \rightarrow M + 2CO_2 \qquad (3)$$

The thermal decomposition of transition metal squarate compounds has not been widely investigated. Like the oxalate

ion (see a. below), the squarate ion (see b. below) forms water insoluble M^{II} (M = Cr, Mn, Fe, Co, Ni, Cu, Zn) compounds, presumed to be polymeric materials. Unlike oxalic acid, which behaves as a weak acid, squaric acid has a pK_a comparable to H_2SO_4. This, coupled with infrared evidence, leads West[10] to suggest the possibility of a pseudo-aromatic nature of the C_4 structure unit. A comparison of the thermal behavior of $M^{II}C_2O_4 \cdot XH_2O$ and $M^{II}C_4O_4 \cdot XH_2O$ is of interest in terms of observing the possible effects of a fundamental difference in the type of bonding of the oxocarbon materials.

STATEMENT OF THE PROBLEM

Thus far there has been no comprehensive study of the thermoanalysis of metal squarates whereas metal oxalates have been investigated widely. However, the parameters reported by each researcher for an individual oxalate were frequently different.

The purpose of this paper is threefold: first, to compare the results of this study of metal oxalates with the results of previous researchers; second, to study the thermal analysis of metal squarates; third, to discover the relationships between initial reaction temperature decomposition and metal radii and activation energies of metal oxalates and squarates.

EXPERIMENTAL

Synthesis of Metal Oxalate Hydrate - Oxalic acid dihydrate, 1.8 grams, was dissolved with 1 ml. of concentrated ammonia solution diluted in 200 ml. of water in an Erlenmeyer flask, 0.015 mole of metal sulphate hydrate was dissolved in about 100 ml. of water, and this solution was added dropwise and with constant stirring to the oxalic acid solution. This solution was allowed to stand until the precipitate had settled (about one-half hour) and then the supernatant liquid was decanted as carefully and completely as possible in order to retain the solid. Fine suspension that was lost in the liquid was ignored as long as the bulk of the solid was retained. The resultant metal oxalate precipitate was added to 50 mg. of oxalic acid dihydrate in 10 ml. of water which was heated almost to boiling. This mixture was then swirled to produce a slurry which was poured equally into two 10 ml. test tubes. For five minutes this solution was centrifuged and then all liquid was discarded. A small amount of distilled water was added and stirred well into each tube to rinse the solid. Then each tube was again centrifuged and the resulting liquid discarded. The rinsing process was repeated twice more. After the final rinse, the

liquid was decanted as completely as possible. Using a clean spatula, the solid was scraped out of the test tubes onto a clean three-inch watch glass. Spread into a thin layer, the product was allowed to dry and then all lumps were crushed with a spatula. The powder was spread into a thin layer on the watch glass, carefully placed in a drawer, and allowed to dry for a week. Filter paper folded in a "v" shape was placed over the powder to protect it from dust.

Synthesis of Chromium^{II} Oxalates[11] - Because of the sensitivity of Chromium^{II} to air oxidation, special synthetic work must be carried on, as described below. Chromium metal, 0.05 mole, was added to 75 ml. of distilled water in 200 ml. triple-necked flask. With the magnetic stirrer, the solution was refluxed under N_2 atmosphere for about ten minutes. By using a syringe, sulfonic acid (H_2NSO_3H) was injected into the flask (Fig. 1) and then carefully 0.05 mole of ammonium oxalate ($(NH_4)_2C_2O_4$) was injected into the flask. Chromium oxalate cannot be filtered from vacuum filtrations so the product was collected by the centrifugal method. The proportion of chromium oxalate can be expressed by the following reaction:

$$CrO + H_2NSO_3H \rightarrow Cr^{II} \text{ (blue)} \qquad (4)$$

$$Cr^{II} + (NH_4)_2C_2O_4 \rightarrow \underset{\text{(green)}}{CrC_2O_4 \cdot XH_2O} + 2NH_4^+ \qquad (5)$$

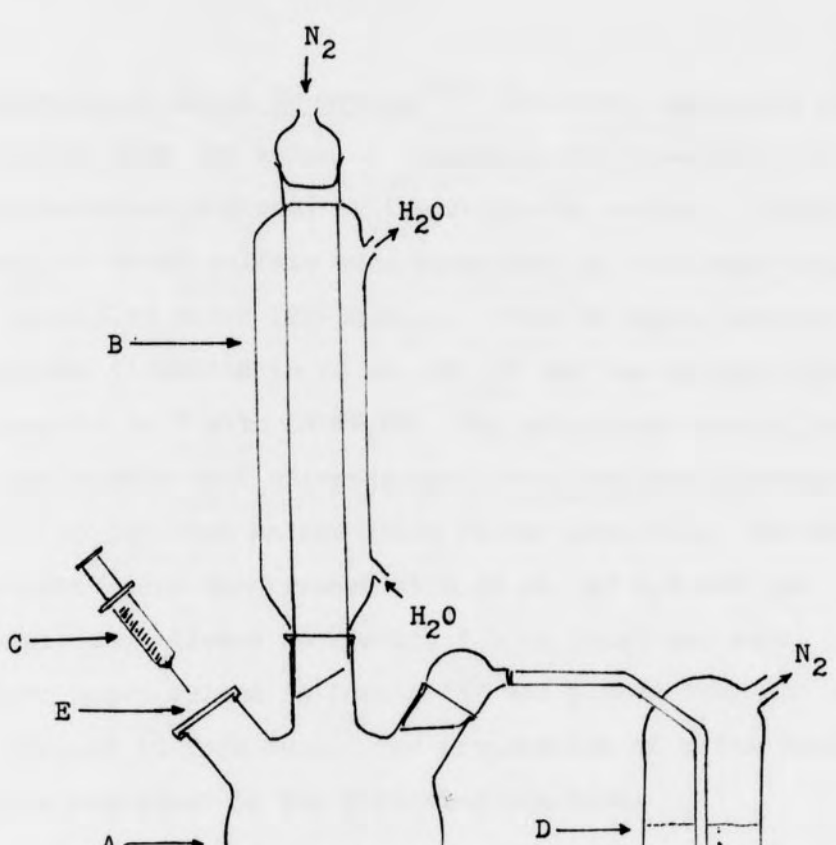


Fig. 1. Diagram and apparatus for the preparation of Cr^{II}oxalate.

A Triple-necked flask

B Condenser

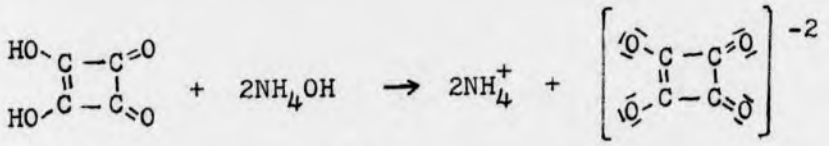
C Syringe

D Bubble indicator

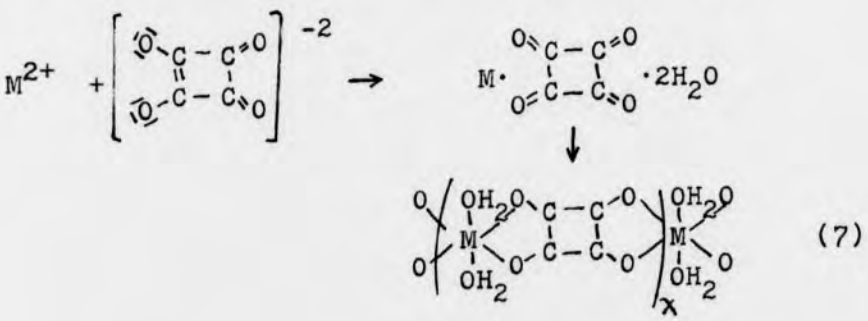
E Septa

F Magnetic stirrer

Synthesis of Metal Squarates[10] - The metal squarates were prepared from the anion of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) by the following method. Twenty mmole of metal sulfate were dissolved in a minimum amount of distilled water (20-30 ml.). Then 20 mmole squaric acid was dissolved in 20 ml. of H_2O and the pH was adjusted carefully to 7 with 6M NH_4OH. The solutions were allowed to mix slowly with stirring until the insoluble product could be isolated on the glass filter crucible. The metal squarates were then washed with 20 ml. of H_2O and the product was allowed to air-dry for at least one week. A filter paper folded to form a "v" was placed over the solid to protect it from dust. The preparation of metal squarates can be expressed by the following reaction:



(6)



(7)

All metal oxalates and squarates obtained were characterized by x-ray powder patterns. Each of the characterizations is very unique. The final product from decomposition from each oxalate and squarate compound also has been characterized by x-ray powder pattern, giving the same result as the pattern of pure metal and metal oxide. For all practical purposes, all three methods of preparation are efficient and often lead to pure products since all metal oxalates and squarates are very insoluble.

Thermal Analysis Equipment - The thermogravimetric (TG) and differential thermogravimetrid analysis (DTG) curves were obtained from a Perkin-Elmer DSC-1b differential scanning calorimeter, and TGS-1 thermal balance. From room temperature to 500°, at a heating rate of 10°/minute in helium atmosphere, the range of 3-6 mg. powdered sample was placed in an Al_2O_3 crucible and used in each measurement. J. A. Dilts, research director, set up and modified all of the TGA equipment for this study. The modification and operating procedures of this equipment were extremely necessary for obtaining an analog data output which is described below.

TGS-1 Thermobalance - The teflon needle valves were used to replace the screw cap closures on the gas inlet and tareloop of the TGS-1 in order to provide the perfect conditions of the atmosphere within the balanced bottle. A small platinum heater was used in the modified furnace mount assembly after the suggestions of Etter and Smith[12]. To avoid the screw closures used by Perkin-Elmer, room temperature vulcanizing silicon elastomer was used to seal these closures at room temperature.

Microcrucibles (Mettler) were used to replace the platinum sample pans provided by Perkin-Elmer. These crucibles were made of hot pressed Al_2O_3 (approximately 150 mg. in

weight). This allowed for small size sample (3-10 mg.). In order to obtain the maximum thermal equilibrium, helium was used as inert gas. Although the rated rings of the Cahn RG balance is 20 micrograms full scale (0.1 microgram sensitivity) in practical terms, the 0.4 mg. range (0.4 microgram sensitivity) represents a maximum sensitivity of this system. Texas Instrument 2 Channel Recorder (Servo-Riter II, 1 millivolt range) or a Multiplexed 4 Channel Heath Recorder was used to record the output from the Cahn RG balance.

The derivative of the primary (attenuated) TG signal is fed into a Cahn Mark II Time Derivative Computer (classical RC differentiation) and the output of this device was recorded on the second channel of the TI Recorder or a second multiplex channel on the Heath Recorder (1 or 10 mv respectively). The approximate ranges on the Time Derivative computers were calibrated by determining weight loss due to diffusion of water vapor from a Kneudsen cell at a controlled temperature. The balance weight ranges were calibrated Class M (NBS) standard 10 mg. weights.

Temperature calibrations of the thermal balance can be obtained by means of the Curie point magnetic transitions in the manual descriptions in the TGS-1. The temperature was found to be within 1^{o} over the temperature range from 100^{o}-500^{o} between the observed and actual temperature.

Auto Range Expander - The operation of the Auto Range Expander was to allow for recording an analog signal at the highest sensitivity without losing information on the recorder. For instance, a sample oxalate might give a 100 mg. weight loss. Without the Auto Range Expander, the maximum range would be 100 mg. full scale on the recorder. This would limit the sensitivity of the recorder to approximately 0.5 mg. With the help of this instrument, a more sensitive range of 10 mg. full could be used with a 0.05 mg. resolution in weight loss. In each incident when the recorder pen reached zero, indicating 10 mg. of weight loss, a precision calibrated offset would be superimposed on the balance signal, returning the pen to the full scale position on the chart (up to 10 times). The sensitivity is therefore 10 times greater than would be the case without using this instrument. In addition, the auto range expander was also useful when studying small weight loss in the presence of large samples, and did not require the specificity in selecting ranges for a determination, especially where it is not possible to anticipate the magnitude of the weight loss associated with the decomposition reaction.

Sample Loading Procedure - The sample crucible was first heated to a temperature of approximately 800° in air, then allowed to cool to room temperature, and suspended from

the balance. The mass dial of RG balance was adjusted so that zero deflection was noted on a recorder scale when the atmosphere of helium had been reestablished in the balance chamber. The sample was then loaded on the balance, being protected from the atmosphere by increasing the flow of helium. An Al_2O_3 top on the crucible was used to prevent the flow of helium from blowing the sample out of the crucible. When the sample was in place and the hangdown tube was returned to its normal position, the helium flow was maintained at 20 ml. per minute for approximately 5 minutes, at which time the balance chamber again contained a pure helium atmosphere. Then the sample weight could be obtained directly from the recorder.

Activation energies obtained by the methods described above are in agreement with published data[13], on the dehydration of $CaC_2O_4 \cdot 2H_2O$ and $ZnC_2O_4 \cdot 2H_2O$, even though smaller samples were used in this study (10 mg. vs. 100 mg.).

RESULTS AND DISCUSSION

Analysis of Thermal Decomposition of Oxalate Compounds - This study is the result of the thermal decomposition of seven compounds and of the products resulting from that decomposition. It is the purpose of this study to discover the relationships between initial reaction temperatures and metal radii and activation energies of the metal oxalates. Of the seven compounds used, five followed the same general pattern of dehydration followed by decomposition while two, copper and chromium, proved to be exceptions to the pattern. The cases of copper and chromium will be examined separately in this study.

The TG and DTG curves of metal oxalates in the temperature range from room temperature to 500° in helium atmosphere are given in Figure 2. The thermoanalysis data obtained is shown in Table 1. The crystallographic radii of the metal ions used are obtained from Shannon and Prewitt.[14]

According to the pyrolysis of all samples and the data obtained, the decomposition of metal oxalates occurs after the dehydration is completed. The oxalates of metal ions with radii larger than cobalt ions decomposed to metal oxides plus equimolar of CO and CO_2. The decomposition temperature

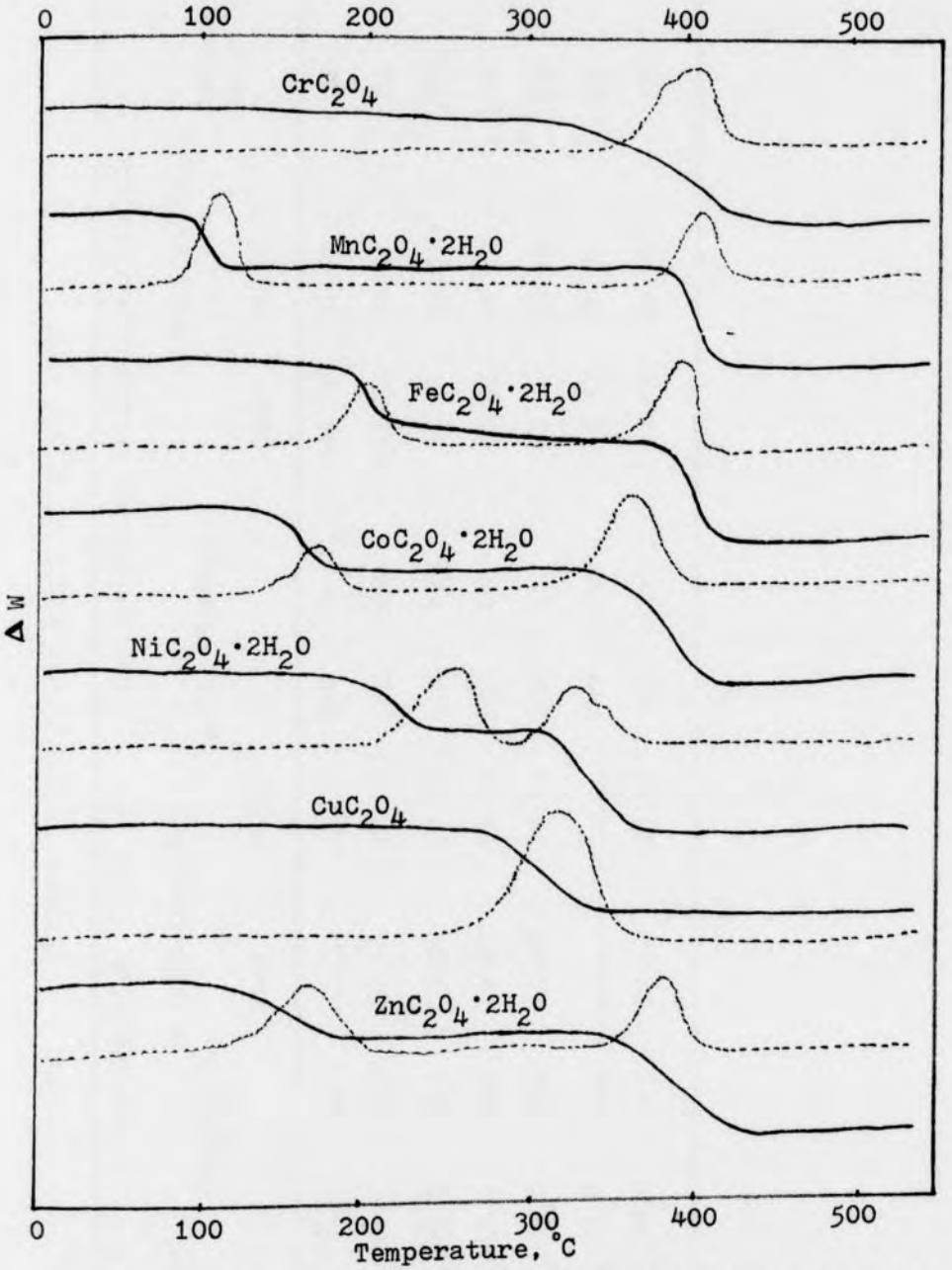


Fig. 2. TG (solid line) and DTG (dotted line) curves of metal oxalates in helium atmosphere.

TABLE 1. THERMAL ANALYSES AND RADII OF METAL IONS

Compound	Dehydration			Decomposition of Anhydrous Oxalate				Radius of Metal Ion/Å
	$T_{(H_2O)}$/°C.	Weight-loss/% obsd	Weight-loss/% calcd	T_d/°C.	Product	Weight-loss/% obsd	Weight-loss/% calcd	
$CrC_2O_4 \cdot 2H_2O$	—	——	——	310	Cr_2O_3	45.70	51.42	.82
$MnC_2O_4 \cdot 2H_2O$	95	20.18	20.12	335	MnO	51.29	50.37	.82
$FeC_2O_4 \cdot 2H_2O$	145	23.40	20.02	310	FeO	46.00	50.05	.78
$CoC_2O_4 \cdot 2H_2O$	125	19.93	19.68	330	Co	60.02	59.89	.74
$NiC_2O_4 \cdot 2H_2O$	150	20.63	19.70	300	Ni	61.36	59.98	.70
$CuC_2O_4 \cdot \frac{1}{2}H_2O$	—	——	——	240	Cu	55.11	58.07	.65
$ZnC_2O_4 \cdot 2H_2O$	85	19.22	19.01	345	ZnO	47.63	46.94	.75

(T_d) seems to be higher than those in the cases of Co, Ni, and Cu which have smaller metal radii. The end products of this group of compounds are found to be pure metals and CO_2. The decomposition reaction of these anhydrous oxalates can be shown as

$$M \cdot C_2O_4 \cdot 2H_2O \rightarrow M \cdot C_2O_4 + 2H_2O \quad (8)$$

$$M \cdot C_2O_4 \rightarrow MO + CO + CO_2 \quad (9)$$

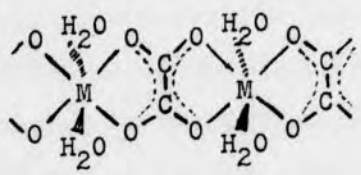
where M = Mn^{II}, Fe^{II}, and Zn^{II}

$$M \cdot C_2O_4 \rightarrow M + 2CO_2 \quad (10)$$

where M = Co^{II}, Ni^{II}, and Cu^{II}

In the case of chromium, the end product of the decomposition is Cr_2O_3, which is the most stable form of chromium oxide.

By using the X-ray deffraction method, J. P. Langries, H. Pezernaut, and J. Pubernot[8] found the structure of the oxalates of Mg, Mn, Fe, Co, and Zn to be polymeric in structure with oxalate ions acting as a quadridentate ligand and water molecules coordinating directly to the metal ions. The structure (see c. below) can be shown to be:



c. Bonding structure of $MC_2O_4 \cdot 2H_2O$

Since water molecules are bonded to the metal ions by electrostatic forces, the initial dehydration temperature ($T_{(H_2O)}$ is considered to reflect the nature of metal-water bond energy. The nature of this relationship should be considered to vary inversely to the size of the metal ions. In other words as the $T_{(H_2O)}$ increases with increasing 1/r. For example, $NiC_2O_4 \cdot 2H_2O$ curve reflects the highest $T_{(H_2O)}$, being 150°, and at the same time contains the smallest ion. Results of the decomposition of metal compounds listed in Table 1 serve to reinforce this theory of bonding. $MnC_2O_4 \cdot 2H_2O$ for instance has the lowest $T_{(H_2O)}$ but the largest radii of the metal ions listed. The two exceptions to this generalization are chromium and copper, which will be dealt with later in this discussion.

From Table 1, studies show that as r increased, T_d decreased so that the bond energy theory becomes applicable to the thermal decomposition of metal oxalates. Examination of Figure 2, the TG and DTG curves of metal oxalate decomposition, serves to support the results recorded in Table 1, which allows the prediction of the metal-oxygen bond strength of the anhydrous oxalates in the following order:

<u>weakest</u> $Cu < Ni < Fe < Cr < Co < Mn < Zn$ <u>strongest</u>

Based on our results of the thermoznalytic data of the oxalate compounds, an attempt to plot $T_{(H_2O)}$ against 1/r was made, but there was no significant linear relationship

in the dehydration process except for decomposition of Co, Ni and Cu as shown in Figure 3. This is in contrast to Nagase's findings[9]. According to his conclusions there were two straight-line relationships in the decomposition processes, the first of which was for the anhydrous oxalates of MN, Fe, and Zn, and the second for the Co, Ni, and Cu species. We cannot duplicate Nagase's results except for the case of Co, Ni, and Cu.

Analysis of Chromium and Copper Oxalate Decomposition Reactions - Of the seven anhydrous oxalates used, two, copper and chromium, reacted differently from the other five compounds. Results from Table 1 show that the dehydration in $CrC_2O_4 \cdot 2H_2O$ and $CuC_2O_4 \cdot \frac{1}{2}H_2O$ is undetectable, whereas initial dehydration temperatures in the other five compounds occur fairly rapidly and can be both detected and predicted. Chromium and copper oxalates, although initially isolated as hydrates, lose their water of hydration on prolonged air drying. Data from Figure 2 shows that the TG and DTG curves of these compounds are markedly different from the curves of the other compounds. It may be assumed from the TG and DTG curves that the relationship of dehydration temperatures and the rate of decomposition of these two oxalates may be different due to a different bonding of the H_2O molecule,

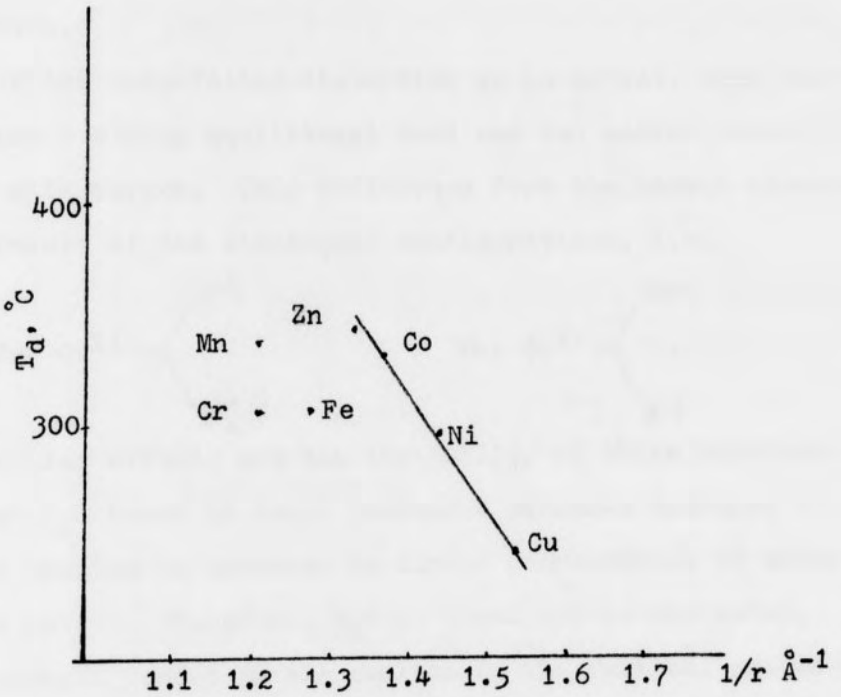
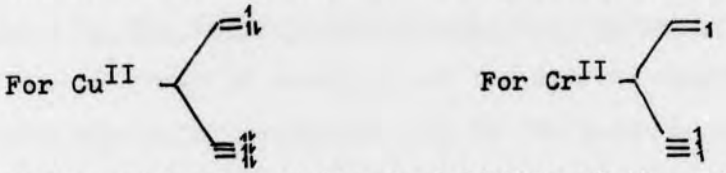


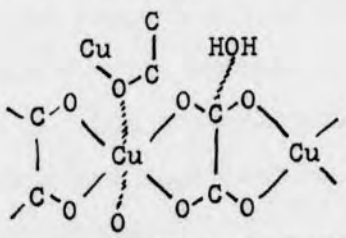
Fig. 3. Relation of initial weight-loss of the decomposition of metal oxalate (T_d) with 1/r.

a bonding which would allow for facile dehydration of H_2O rather than for the gradual dehydration of the other five compounds. A possible explanation of this difference probably lies in the Jahn-Teller effects on molecular structure.

If the Jahn-Teller distortion is in effect, then the Cu forms a strong equilateral bond and two weaker axial bonds with oxygen. This difference from the normal structure is a result of the electronic configurations, i.e.



Jahn-Teller effects and the instability of these hydrates suggest H_2O bound in these complexes involves hydrogen bonded species in contrast to direct coordination of water to the metal. Therefore, H_2O is bound not to the metal, but hydrogen bonded to the oxalate in the vertical pseudo-octohedral structures of CuC_2O_4 (see <u>d.</u> below).



<u>d.</u> Bonding structure of $CuC_2O_4 \cdot \frac{1}{2}H_2O$

Thus, the dehydration of H_2O would occur in a different way because bond linkage is different. Water linked electrostatically to other than the metal ion in the molecule would mean the bonding is weaker than in other compounds where the strength of bonding lies in the relation to the radii of the metal ion. Due to weak bonding the H_2O would logically dehydrate spontaneously when heat is applied so that no dehydration temperatures or weight-loss is observed.

Analysis of the Thermal Decomposition of Squarate Compounds - This second phase of study is of the thermal decomposition of seven squarate compounds. It is the purpose of this second phase to discover the relationships between initial reaction temperatures of metal radii and activation energies of the metal squarates. Each of the compounds followed the general pattern of first dehydration and subsequent decomposition of the squarate.

The TG and DTG curves of metal squarates in the temperature range from room temperature to 500° in helium atmosphere are given in Figure 4. The thermal analysis data obtained is shown in Table 2. The crystallographic radii of the metal ions were obtained from Shannon and Prewitt[14] as in the cases of the oxalates.

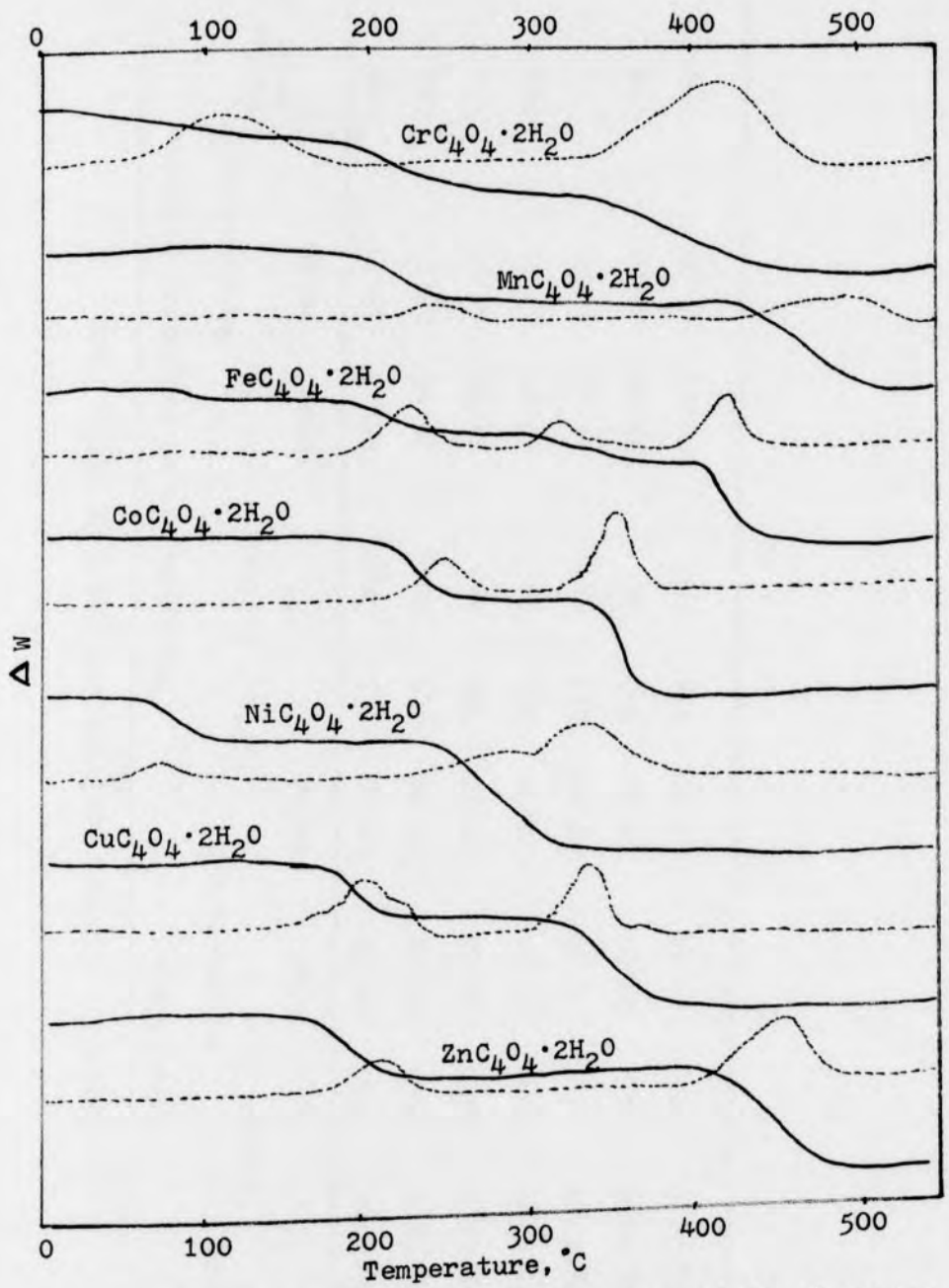


Fig. 4. TG (solid line) and DTG (dotted line) curves of metal squarates in helium atmosphere.

TABLE 2. THERMAL ANALYSES AND RADII OF METAL IONS

Compound	Dehydration			Decomposition of Anhydrous Squarate				Radius of Metal Ion/Å
	$T_{(H_2O)}$/°C.	Weight-loss/%		T_d/°C.	Product	Weight-loss/%		
		obsd	calcd			obsd	calcd	
$CrC_4O_4 \cdot 2H_2O$	75	18.00	17.14	315	Cr_2O_3	46.75	51.22	.82
$MnC_4O_4 \cdot 2H_2O$	190	17.77	17.74	425	MnO_2	26.08	33.50	.82
$FeC_4O_4 \cdot 2H_2O$	168	19.28	17.66	320	FeO	59.40	50.04	.78
$CoC_4O_4 \cdot 2H_2O$	186	17.31	17.39	333	Co	57.17	65.52	.74
$NiC_4O_4 \cdot 2H_2O$	64	6.79	9.54	215	Ni	69.59	65.61	.70
$CuC_4O_4 \cdot 2H_2O$	145	19.89	17.02	310	Cu	59.89	63.80	.73
$ZnC_4O_4 \cdot 2H_2O$	178	18.14	16.87	435	ZnO	40.54	47.36	.75

According to the data obtained, the decomposition of metal squarates occurs after dehydration is completed. The squarates of Co, Ni, and Cu decomposed to pure metals while the squarates of Cr, Mn, Fe, and Zn decomposed to metal oxides plus carbon which could be seen in the crucible, like the oxalates which decomposed to metal oxides and a mixture of CO and CO_2. Only with Co, Ni, and Cu was there any linear relationship between the size of the metal ion radii and the initial reaction temperature. The dehydration reaction of these squarates can be shown as

$$M \cdot C_4O_4 \cdot 2H_2O \rightarrow M \cdot C_4O_4 + 2H_2O \qquad (11)$$

and the decomposition reaction of anhydrous squarates can be shown as

$$M \cdot C_4O_4 \rightarrow M + 4CO \qquad (12)$$

where M = Co, Ni and Cu

$$M \cdot C_4O_4 \rightarrow MO + C + 3CO \qquad (13)$$

where M = Fe and Zn

In the cases of Cr and Mn, the end product is Cr_2O_3 for the former and MnO_2 for the latter.

West, in his studies at the University of Wisconsin, proved that $MC_4O_4 \cdot 2H_2O$ is a dihydrate polymer with squarate ions acting as a chelating agent[10].

Since water molecules are bonded by electrostatic forces, it was assumed that the $T_{(H_2O)}$ would reflect the nature of metal ions and bond energy. However, in only

three squarate compounds was there any relation between the size of the metal ion radii to the $T_{(H_2O)}$. Rather than an inverse relationship, the data obtained showed that the $T_{(H_2O)}$ was in direct proportion to the size of the metal ion radii. For instance, in $NiC_4O_4 \cdot 2H_2O$, which exhibits the smallest radii, the lowest $T_{(H_2O)}$ is found, and vice-versa in the case of Mn. This may be due to the fact that squarate structure is reacting as pseudo aromatic nature which increases the M-O bond strength. Results of the decomposition reactions recorded in Table 2 show a relationship only for three squarates, Co, Ni, and Cu. According to the data obtained, this relationship does not exist in the cases of Cr, Mn, Fe, and Zn. The radii of Cu in Table 1 are different from from Table 2 because of the difference in coordination number between oxalates and squarates.

An attempt to plot $T_{(H_2O)}$ and T_d versus 1/r was made and there were found two straight-line relationships between Cu, Co, and Ni, whose decomposition had revealed a relationship between radii size and both $T_{(H_2O)}$ and T_d. There was no relationship found in the plotting of the other squarates. Plotting data is recorded in Figures 5 and 6. Examination of both Figures indicates the absence of a notable relationship of any kind in the other four squarate

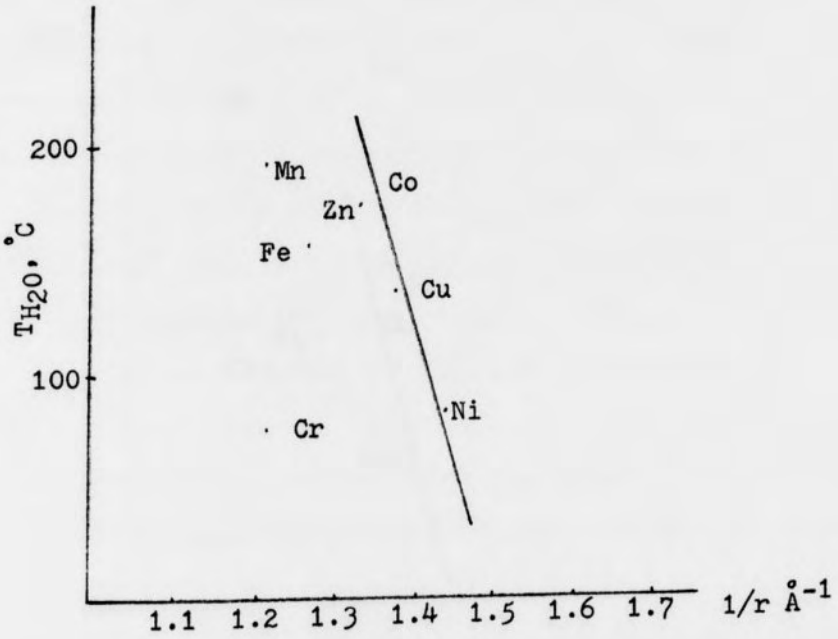


Fig. 5. Relation of initial weight-loss of the dehydration of metal squarates (T_{H_2O}) with 1/r.

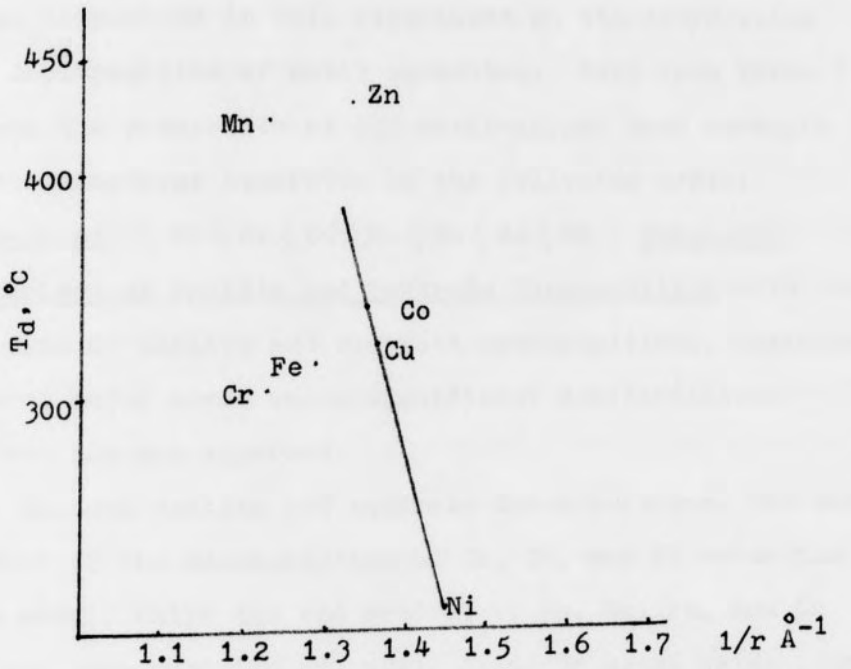


Fig. 6. Relation of initial weight-loss of the decomposition of metal squarates (T_d) with 1/r.

decompositions. Activation energies were obtained from TG and DTG data using the methods of Coats and Redfern[15], Freeman and Carroll[16], and Tang[17]. In each case, a plot of the activation energy vs. 1/r revealed the same relationships determined in this experiment on the dehydration and decomposition of metal squarates. Data from Table 2 allows the prediction of the metal-oxygen bond strength of the anhydrous squarates in the following order:

Weakest $<$ Ni $<$ Cr $<$ Cu $<$ Fe $<$ Zn $<$ Co $<$ Mn Strongest

Comparison of Oxalate and Squarate Decomposition - In comparing data of oxalate and squarate decompositions, there are several major areas where significant similarities or differences are apparent.

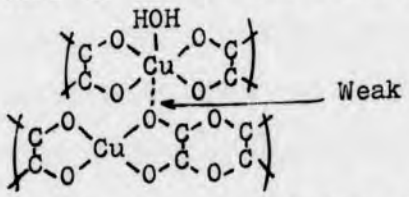
In both oxalate and squarate decompositions, the end product of the decomposition of Co, Cu, and Ni materials was pure metal, while the end product of Cr, Mn, Fe, and Zn oxalate decomposition was metal oxide or metal oxide plus carbon in the cases of Cr, Mn, Fe, and Zn squarates.

The decomposition of oxalate compounds revealed inverse proportionality between the size of the metal ion radii and $T_{(H_2O)}$. Only in the decomposition of Cu, Co, and Ni squarates was there any $T_{(H_2O)}$-metal radii linear relationship. The order in the squarate case was Ni Cu Co, and for the oxalates, a different order was observed (Cu Ni Co).

Initial dehydration temperatures ranged from room temperature to 150° in oxalate decomposition and from 75° to 190° in squarate decomposition. Likewise, decomposition temperatures were notably higher in squarate decomposition than in oxalate decomposition.

A possible explanation of the difference in heat required for squarate decomposition over that required for oxalate decomposition lies in the structure of the ion and the resultant bonding of H_2O to that ion. Examination of the TG and DTG curves of the two sets of compounds reveals stronger bonding of H_2O in the squarates is found even in the case of Cr and Cu which were exceptions in the oxalate data. $CrC_4O_4 \cdot 2H_2O$ shows differences from other squarates, but unlike $CrC_2O_4 \cdot 2H_2O$, a distinct dehydration temperature can be seen, thus reinforcing the theory of stronger bonding of H_2O even in Cr.

In the case of $CuC_2O_4 \cdot \frac{1}{2}H_2O$ as compared to $CuC_4O_4 \cdot 2H_2O$ insights into structure and bonding may be discovered. One possible structure of copper oxalate ions (see e. below) reveals that it consists of three types of possible bonding within the structure of the ion as shown below:



e. Bonding Structure of $CuC_2O_4 \cdot \frac{1}{2}H_2O$

The weakest bond in this structure is the bond between the Cu ion and the oxygen from the other oxalate ion which could create a 5-coordination if this bond were to be broken.

The physical appearance of copper oxalate indicates a possible 6-coordination by its color. Copper oxalate is blue, while copper squarate is yellow in color. $Cu(NH_3)_4SO_4$ and $Cu(NH_3)_4Cl_2$ which are both 6-coordinate, are blue in color whereas $Cu(NH_3)_2Cl_2$ is yellow and is 4-coordinate. At room temperature $CuC_4O_4 \cdot 2H_2O$ does have normal Cu^{II} magnetic moment which indicates a d^9 system (this information was obtained by the determination in private communication with Dr. A. L. Crumbliss of Duke University). Therefore, the structure of $CuC_4O_4 \cdot 2H_2O$ might be 4-coordinate by the nature of its color, and it is possible that this appearance is reflected by the delocalization in the molecule. We suggest that the structure of $CuC_4O_4 \cdot 2H_2O$ appears to be square planar geometry over pseudo octahedral, and octahedral for CuC_2O_4.

West has proven that divalent metals react with squarate ions to give dihydrate polymers having the formula $MC_4O_4 \cdot 2H_2O$ in his studies on resonance stabilized cyclic oxyanions. Thus, such a ligand as found in $CuC_4O_4 \cdot 2H_2O$ might allow for a charge transfer from copper to copper which is not possible for oxalate in $CuC_2O_4 \cdot \frac{1}{2}H_2O$. Because of the possibility

of charge transfer and a resonance stabilized ligand, more energy would be required to break the bonding in the squarates than in the oxalates.

A very interesting point was found in the case of decomposition of MnC_2O_4 and MnC_4O_4. The end product is MnO for MnC_2O_4 but MnO_2 for MnC_4O_4. The study shows that manganese is oxidized from Mn^{II} to Mn^{IV} in case of MnC_4O_4. The explanation can be shown by the following equation:

$$MnC_4O_4 \rightarrow MnO_2 + 2CO + 2C \qquad (14)$$

The reactions are:

$$Mn^{+2} = Mn^{+4} + 2e^-$$

$$2C^{+1.5} + 3e^- = 2C$$

$$2C^{+1.5} = 2C^{+2} + e^-$$

$$\text{Net} \quad Mn^{+2} + 4C^{+1.5} = Mn^{+4} + 2C^{+2} + 2C \qquad (15)$$

The results of activation energy from kinetic study of thermal analysis of metal oxalates and squarates are given in Tables 3 and 4. The results in Table 3 were selected from the best correlation coefficients which determined the reaction order using the Coats and Redfern method. The results in Table 4 were obtained by using the best correlation coefficient from Freeman-Carroll or Tang methods.

From the kinetic data, we found that the $T(H_2O)$ in oxalates and squarates is ranging approximately 20 kcal/mole from one compound to another. The activation energies by

TABLE 3. ACTIVATION ENERGY OF DIFFERENT METAL OXALATE AND SQUARATE COMPOUNDS BY COATS AND REDFERN METHOD

	Thermal Dehydration kcal/mole				Thermal Decomposition kcal/mole			
Metal	Oxalate	Order of Reaction	Squarate	Order of Reaction	Oxalate	Order of Reaction	Squarate	Order of Reaction
Cr	_____	_	-14.87	1	-26.61	0	-18.58	0
Mn	(NA)	1	-26.37	0	-41.91	0	-76.49	1
Fe	-15.44	1	-24.74	1	-33.45	1	-76.31	1
Co	-27.79	1	-18.25	1	-74.54	0	-67.22	0
Ni	-21.80	0	-17.39	0	-60.18	1	-18.59	1
Cu	_____	_	-26.01	0	-113.42	0.5	-32.14	0
Zn	-20.50	1	-19.77	0	-58.85	0.5	-90.75	0

TABLE 4. ACTIVATION ENERGY OF DIFFERENT METAL OXALATE AND SQUARATE COMPOUNDS BY FREEMAN-CARROLL AND TANG METHODS

	Thermal Dehydration kcal/mole		Thermal Decomposition kcal/mole	
Metal	Oxalate	Squarate	Oxalate	Squarate
Cr	_____	-13.43	-57.09	-34.34
Mn	(NA)	-40.23	-61.03	-60.26
Fe	-14.49	-13.02	-49.70	-83.79
Co	-16.54	-28.00	-88.47	-119.47
Ni	-28.89	-12.31	-52.53	-27.27
Cu	_____	-19.01	-132.25	-28.76
Zn	-29.14	-25.00	-115.00	-87.94

isothermal methods of ZnC_2O_4 by decomposition were reported by T. Palanisamy[18] as -60.8 and -62.7 kcal/mole and by dynamic methods (Coats and Redfern) as -52.0 kcal/mole, whereas our own result is -58.85 kcal/mole. T. Palanisamy reported the activation energy of $ZnC_2O_4 \cdot 2H_2O$ dehydration calculated by Coats and Redfern's method as 17.0 kcal/mole. The result found in our study is 20.50 kcal/mole.

Figure 7 shows the plot of dehydration activation energies for metal squarates vs. 1/r from Freeman-Carroll and Tang methods. Figure 8 shows the plot of decomposition activation energies of metal squarates from Freeman-Carroll and Tang methods. In both cases the straight-line relationship was found only in Co, Ni, and Cu.

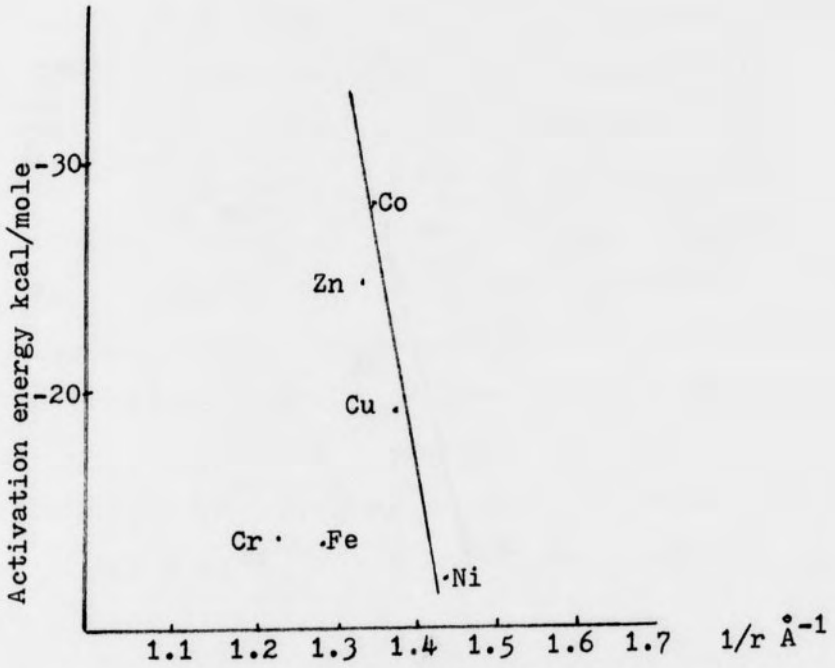


Fig. 7. Relation of dehydration activation energy of metal squarates by F-C/Tang method with 1/r.

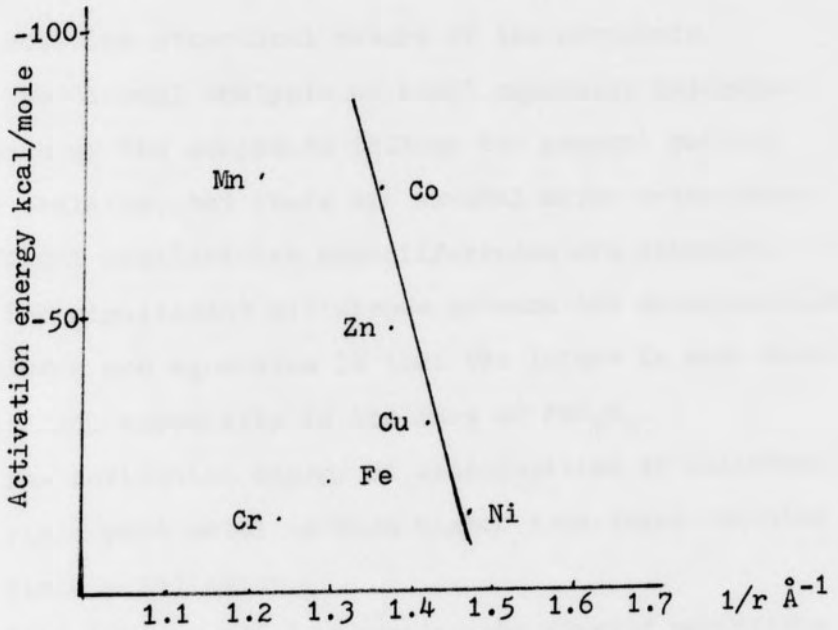


Fig. 8. Relation of decomposition activation energy of metal squarates by C-R method with 1/r.

SUMMARY

In the first part of this study we found some similarities as well as contradictions in oxalate compounds with previous researchers. The bonding theory was applied to discuss the structural nature of the compounds.

The thermal analysis of metal squarates indicates that each of the compounds follows the general pattern of the oxalates, but there are several major areas where significant similarities and differences are apparent.

The significant difference between the decomposition of oxalates and squarates is that the latter is much more complicated, especially in the case of FeC_4O_4.

The activation energy of decomposition of oxalates which yield pure metal is much higher than those oxalates which yield metal oxide.

This is an initial report of the kinetic parameters for the first transition series of metal squarates. From the results of our kinetic data, we found that there is a small variation in all three methods of calculation.

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APPENDIX

The computer programs basically calculate x and y points according to the equations using the Freeman-Carroll method and the method of Tang, and perform at least squares regression analysis from which the activation energy and, in the case of the Freeman-Carroll method, the order for the solid state thermal decomposition. In addition provision has been made for listing the observed x and y values as well as the calculated y values and deviations. Once a data set has been typed in it may be saved on a file for future use or output on paper tape. Once data has been saved, it may be modified, recalled to the main program, and recalculated. Provision has also been made to plot data, either on the teletype or on the TSP plotter.

The program is written in the basic language and is compatible with the Systems 72 and Hewlett-Packard computer.

```
TKIN

9  COM X[100],Y[100],N,X$[72]
10  REM THIS VERSION WAS MODIFIED ON 21 FEBRUARY BY J A DILTS
11  REM THIS PROGRAM IS A COMBINATION FREEMAN CAROLL KINETICS
12  REM AND TANG'S METHOD FOR DETERMINING THE APPARENT
13  REM ORDER OF REACTION OF TG AND DTG DATA.  USED ALSO
14  REM IS A PLOTTING ROUTINE :LINPLT- A CHAINED PROGRAM
15  REM WHICH WILL GIVE A PLOT OF THE APPROPRIATE ACTIVATION
16  REM ENERGY PARAMETERS-THIS ROUTINE WAS WRITTEN BY J M SCHOMYER
17  PRINT
18  PRINT
19  PRINT
20  PRINT
30  PRINT "TG/DTG ACTIVATION ENERGY AND RXN. ORDER PROGRAM"
40  PRINT "THE FIRST CALCULATION IS THE FREEMAN CAROLL METHOD"
70  DIM Q[100],Z[100],O[100],V[100]
90  DIM K[100],L[100],U[100]
95  FILES TG
100  DIM A$[60]
101  DIM T$[72]
110  LET D=E=F=G=H=I=J=0
111  PRINT "IS DATA ON FILE TG(Y OR N)";
112  INPUT T$
113  IF T$[1,1]="Y" THEN 510
120  PRINT "FORMULA OF COMPOUND OR END"
130  INPUT A$
140  IF A$="END" THEN 1090
150  PRINT " PLEASE TYPE IN THE NUMBER OF OBSERVATIONS"
160  INPUT N
170  IF N=0 THEN 1090
180  PRINT "WHAT IS THE SAMPLE WT IN MG";
190  INPUT D
200  PRINT "WHAT IS THE FINAL WT. IN MG.";
```

```
210  INPUT G
220  PRINT "WHAT IS THE INITIAL TG READING (0-1)";
230  INPUT H
240  PRINT "WHAT IS THE DTG RANGE IN MG/MIN";
250  INPUT J
260  PRINT "WHAT IS THE TG RANGE IN MG";
270  INPUT F
271  READ #1,1
275  PRINT #1;A$,N,D,G,H,J,F
280  PRINT "ENTER DATA ON THE FORMAT:TG,DTG(0-1),T(IN DEG C)"
290  FOR I=1 TO N
300  PRINT "DATA";
310  INPUT K[I],L[I],U[I]
314  PRINT #1;K[I],L[I],U[I]
320  LET V[I]=1/(U[I]+273.15)
330  O[I]=((D-G)-(H*F-K[I]*F))
340  LET L[I]=L[I]*J*.86667
350  NEXT I
360  FOR I=1 TO N-1
370  LET Y[I]=(LOG(L[I])-LOG(L[I+1]))/(LOG(O[I])-LOG(O[I+1]))
380  LET X[I]=(V[I]-V[I+1])/((LOG(O[I]))-(LOG(O[I+1])))
390  NEXT I
400  LET N=N-1
405  LET X$="FREEMAN-CAROLL CALCULATION"
410  REM THERE WILL BE N-1 VARIABLES IN THE DIFFERENCE CALC
411  CHAIN "LINPLT"
421  PRINT "TANG(T),RESTART(S),END(E),DUMP DATA(D),REPLT(R)";
422  INPUT T$
423  IF T$[1,1]="T" THEN 440
424  IF T$[1,1]="S" THEN 30
425  IF T$[1,1]="D" THEN 600
426  IF T$[1,1]="R" THEN 700
427  GOTO 1090
440  READ #1,1
```

```
441  READ #1;A$,N,D,G,H,J,F
442  FOR I=1 TO N
443  READ #1;K[I],L[I],U[I]
444  NEXT I
445  FOR I=1 TO N
450  Y[I]=LOG((L[I]*J*.86667)/((D-G)-(H*F-K[I]*F)))
451  X[I]=1/(U[I]+273.15)
452  NEXT I
455  LET X$="TANG CALCULATION"
500  CHAIN "LINPLT"
510  READ #1,1
520  READ #1;A$,N,D,G,H,J,F
525  FOR I=1 TO N
530  READ #1;K[I],L[I],U[I]
535  NEXT I
540  FOR I=1 TO N
545  V[I]=1/(U[I]+273.15)
550  O[I]=((D-G)-(H*F-K[I]*F))
555  LET L[I]=L[I]*J*.86667
560  NEXT I
565  GOTO 360
600  PRINT "DUMP TO TAPE(T) OR FILETG2(F1) OR FILE T(F2)";
610  INPUT T$
620  IF T$="T" THEN 640
621  IF T$="F1" THEN 630
622  CHAIN "COPY-3"
630  CHAIN "TGDUM"
640  CHAIN "X-FUN"
700  CHAIN "LINPLT",910
1090  END
```

COPYZ3

```
10  REM THIS PROGRAM TRANSFERES DATA FROM
20  REM A RANDOM ACCESS FILE TO A SERIAL
30  REM ACCESS FILE
40  REM NEEDS MODIFICATION IF FILE#1 HAS MORE THAN ONE RECORD
50  REM SUITABLE AT PRESENT ONLY FOR TG/DTG KINETICS USE
60  REM
70  REM
80  REM
90  REM
100  Q=0
110  Z=1
120  FILES TG,T
130  DIM B$[72]
140  READ #2,Z
150  Q=0
160  GOTO TYP(-2) OF 170,190,240,220
170  READ #2;Y
180  GOTO 160
190  READ #2;B$
200  Q=Q+1
210  GOTO 160
220  Z=Z+1
230  GOTO 140
240  READ #2,Z
250  GOTO TYP(-2) OF 260,290,350,350
260  READ #2;Y
270  GOTO 250
280  GOTO 350
290  FOR C=1 TO Q
300  READ #2;B$,N,D,G,H,J,F
```

```
310  FOR I=1 TO 3*N
320  READ #2;X[I]
330  NEXT I
340  NEXT C
350  M=N=D=G=H=J=F=0
360  M=1
370  DIM A$[72]
380  DIM X[100]
390  IF  END #1 THEN 480
400  IF  END #2 THEN 500
410  READ #1;A$,N,D,G,H,J,F
420  PRINT #2;A$,N,D,G,H,J,F
430  FOR I=1 TO 3*N
440  READ #1;X[I]
450  PRINT #2;X[I]
460  NEXT I
470  PRINT #2; END
480  PRINT "TRANSFER TO FILE T COMPLETE"
485  PRINT "LAST TRANSFER TO RECORD "Z" OF FILE T"
490  GOTO 510
500  PRINT "PHYSICAL END OF SERIAL ACCESS FILE"
501  PRINT "FILE T IS FULL. PLEASE DUMP FILE T ON TAPE USING"
502  PRINT "THE SYSTEM PROGRAM CALLED LODUMP. TO GET THIS TYPE"
503  PRINT "GET-$LODUMP AND ANSWER TO FILE NAME,T"
504  PRINT "BRING TAPED FILE TO JAD BEFORE MODIFYING THE CONTENTS"
505  PRINT "OF FILE T. THANK YOU!!!"
510  CHAIN "TKIN"
520  END
```

```
LINPLT

9  COM X[100],Y[100],N,X$[72]
10  DIM A$[50],B$[50],C$[50]
20  DIM D$[50]
25  FILES TG
26  DIM Z$[72]
120  PRINT
140  DIM S[100],T[100]
150  DIM Q[100],Z[100]
160  PRINT
190  IF N=0 THEN 2060
260  X[N+1]=-1.E+08
320  Y[N+1]=-100000.
330  LET T=W=P=T2=0
340  W2=0
350  REM T IS THE SUM OF THE INDEPENDENT VARIABLERS
360  REM W IS THE SUM OF THE DEPENDENT VARIABLES
370  REM P IS THE SUM O THE CORSS PRODUCTS
380  REM T2 IS THE SUM OF THE SWUARES OF THE INDP VARIABLES
390  FOR I=1 TO N
400  T=T+X[I]
410  T2=T2+X[I]^2
420  W=W+Y[I]
430  P=P+X[I]*Y[I]
440  W2=W2+Y[I]^2
450  NEXT I
460  B$="Y"
480  IF B$[1,1]="Y" THEN 520
490  A=0
500  GOTO 540
510  REM SOLVE FOR THE COEFFICIENTS BY USING MORMAL EQUATIONS FOR
520  A=1
530  REM THE LEAST SQUARE LINE
```

```
540  IF A=0 THEN 570
550  B=(W*T2-T*P)/(N*T2-T^2)
560  GOTO 580
570  B=0
580  IF A=0 THEN 610
590  M=(N*P-T*W)/(N*T2-T^2)
600  GOTO 611
610  M=P/T2
611  READ #1,1
612  READ #1;Z$
613  PRINT TIM(2)"/"TIM(3)"*"TIM(1)":"TIM(0)
614  PRINT X$
615  PRINT "FOR "Z$" THE FOLLOWING KINETIC PARAMETERS HAVE BEEN CALCULATED"
616  PRINT
620  PRINT "Y = MX +B"
630  PRINT "B="B"M="M
631  A1=0
632  A1=((M*1.987)/(1000))
633  PRINT " THE APPARENT ACTIVATION ENERGY IS "A1" KCAL/MOLE"
634  IF X$[1,1]="T" THEN 640
635  PRINT " THE APPARENT ORDER OF REACTION IS "B
640  LET S=0
650  FOR I=1 TO N
660  Z[I]=B+M*X[I]
670  Q[I]=Y[I]-Z[I]
680  S=S+Q[I]*Q[I]
690  NEXT I
700  IF A=0 THEN 730
710  LET R=SQR(S/(N-2))
720  GOTO 740
730  R=SQR(S/(N-1))
740  IF A=0 THEN 770
750  M1=R*SQR(N/(N*T2-T^2))
760  GOTO 780
```

```
770  M1=SQR((W2-M*P)/((N-1)*T2))
780  IF A=0 THEN 810
790  B1=R*SQR(T2/(N*T2-T^2))
800  GOTO 820
810  B1=0
815  PRINT
820  PRINT ""
821  PRINT "STANDARD DEVIATIONS ARE:"
830  PRINT "SB="B1"SM="M1
835  PRINT "STD. DEV. IN ACTIVATION ENERGY IS +/-"M1*1.98/1000
840  IF A=0 THEN 880
850  C=(N*P-T*W)
860  C=C/SQR((N*T2-T^2)*(N*W2-W^2))
870  GOTO 890
880  C=P/SQR(T2*W2)
890  PRINT "CORRELATION COEFF. IS "C
900  PRINT
910  PRINT "DO YOU WANT A TABLE, GRAPH, BOTH, OR NEITHER";
920  INPUT B$
925  READ #1,1
926  READ #1;Z$
930  GOSUB 1060
940  IF K9=4 THEN 1790
950  IF K9#2 THEN 980
960  GOSUB 1210
970  GOTO 160
980  PRINT
990  PRINT "OBSERVED X   OBSERVED Y   CALCULATED Y   RESIDUAL"
1000  FOR I=1 TO N
1010  PRINT USING "SD.2DE,4X,SD.2DE,5X,SD.2DE,5X,SD.2DE";X[I],Y[I],Z[I],Q[I]
1020  NEXT I
1030  IF K9#3 THEN 1050
1040  GOSUB 1210
```

```
1050  GOTO 1790
1060  IF B$[1,1]="T" THEN 1130
1070  IF B$[1,1]="G" THEN 1150
1080  IF B$[1,1]="B" THEN 1170
1090  IF B$[1,1]="N" THEN 1190
1100  PRINT "'T', 'G', 'B', OR 'N'";
1110  INPUT B$
1120  GOTO 1060
1130  K9=1
1140  GOTO 1200
1150  K9=2
1160  GOTO 1200
1170  K9=3
1180  GOTO 1200
1190  K9=4
1200  RETURN
1210  FOR I=1 TO N
1220  FOR J=I+1 TO N
1230  IF Y[I]>Y[J] THEN 1300
1240  Q3=Y[J]
1250  Y[J]=Y[I]
1260  Y[I]=Q3
1270  Q3=X[J]
1280  X[J]=X[I]
1290  X[I]=Q3
1300  NEXT J
1310  NEXT I
1320  PRINT '10'10
1330  PRINT "WHAT ARE THE MIN. AND MAX. X VALUES FOR THE GRAPH";
1340  INPUT R2,R1
1350  PRINT "WHAT ARE THE MIN. AND MAX. Y VALUES FOR THE GRAPH";
1360  INPUT R4,R3
1370  PRINT "WHAT IS THE Y STEP";
1380  INPUT R5
```

```
1390  FOR I=1 TO N
1400  IF Y[I] <= R3 THEN 1420
1410  NEXT I
1420  J=I
1430  A$="-"
1440  C$="SD.2DE,A       "
1450  B$="*"
1480  PRINT
1490  PRINT "-------------------------------------------------------------------------------------------------------------------"
1500  R6=R2
1510  PRINT
1511  PRINT X$
1515  PRINT TIM(2)"/"TIM(3)"*"TIM(1)":"TIM(0)"-"Z$
1516  PRINT
1520  PRINT TAB(33)"X-AXIS"
1530  PRINT  USING "#,5X,SD.2DE";R6
1540  FOR I=1 TO 5
1550  R6=R6+(R1-R2)/5
1560  PRINT  USING "#,X,SD.2DE";R6
1570  NEXT I
1580  PRINT "          +-----+-----+-----+-----+-----+-----+-----+-----+-----+-----+"
1590  FOR I=R3 TO R4 STEP -R5
1600  C$[9,14]="      "
1610  IF Y[J] >= I AND Y[J] <= I+.5*R5 THEN 1830
1620  IF Y[J]<I AND Y[J]>I-.5*R5 THEN 1830
1630  PRINT  USING C$;I,A$
1640  NEXT I
1650  PRINT "          +-----+-----+-----+-----+-----+-----+-----+-----+-----+-----+"
1660  R6=R2
1670  PRINT  USING "#,5X,SD.2DE";R6
1680  FOR I=1 TO 5
1690  R6=R6+(R1-R2)/5
1700  PRINT  USING "#,X,SD.2DE";R6
1710  NEXT I
```

```
1720  PRINT
1730  PRINT TAB(33)"X-AXIS"
1740  PRINT
1750  PRINT "----------------------------------------------------------------------------------------------------------------------------------"
1760  PRINT
1770  PRINT
1780  PRINT
1790  CHAIN "TKIN",421
1800  INPUT B$
1810  IF B$[1,1]$"Y" THEN 2060
1820  RETURN
1830  D$="123456789"
1840  C$[12,14]="X,A"
1850  C$[9,9]=","
1860  X=R2
1870  FOR K=0 TO 50
1880  IF X[J] <= X+.5*(R1-R2)/50 THEN 1930
1890  X=X+(R1-R2)/50
1900  NEXT K
1910  J=J+1
1920  GOTO 1630
1930  IF K-INT(K/10)*10$0 THEN 1970
1940  IF K=0 THEN 2030
1950  C$[11,11]="0"
1960  GOTO 1980
1970  C$[11,11]=D$[K-INT(K/10)*10,K-INT(K/10)*10]
1980  IF K<10 THEN 2000
1990  C$[10,10]=D$[INT(K/10),INT(K/10)]
2000  PRINT  USING C$;I,A$,B$
2010  J=J+1
2020  GOTO 1640
2030  C$[12,13]="  "
2040  GOTO 2000
2050  GOTO 2060
2060  END
```

TGDUM

```
10  REM PROGRAM TO DUMP DATA FROM FILE TG ONTO TG2
20  DIM X[100]
30  DIM A$[72],B$[72]
40  FILES TG,TG2
45  M=0
50  READ #1,1
70  READ #1;A$,N,D,G,H,J,F
80  FOR I=1 TO 3*N
90  READ #1;X[I]
100  NEXT I
110  PRINT
120  READ #2,1
130  GOTO TYP(2) OF 140,160,180
140  READ #2;Y
150  GOTO 130
160  READ #2;B$
170  GOTO 130
175  PRINT "COPY FILE FULL"
176  STOP
180  IF  END #1 THEN 175
199  PRINT #2;A$,N,D,G,H,J,F
200  FOR I=1 TO 3*N
210  PRINT #2;X[I]
220  NEXT I
230  PRINT "TRANSFER OF DATA FOR "A$"  TO TG2 COMPLETE"
240  STOP
250  END
```

TGPURG

```
10  DIM A$[72],B$[72],C$[72],D$[72]
20  DIM X[100]
30  PRINT "CODE";
40  INPUT D$
50  IF D$#'8'9'20 THEN 420
60  PRINT "NAME OF DATA SET TO BE PURGED"
70  INPUT C$
80  FILES TG2,TG2
90  READ #1,1
100  READ #2,1
105  M=0
106  Q=0
110  IF TYP(1)=3 THEN 380
120  READ #1;A$
130  IF A$=C$ THEN 240
140  READ #2;A$
150  READ #1;N,D,G,H,J,F
160  READ #2;N,D,G,H,J,F
170  FOR I=1 TO 3*N
180  READ #1;X[I]
190  NEXT I
200  FOR I=1 TO 3*N
210  READ #2;X[I]
220  NEXT I
225  M=M+1
230  GOTO 110
240  READ #1;N,D,G,H,J,F
250  FOR I=1 TO 3*N
260  READ #1;X[I]
270  NEXT I
```

```
275  M=M+1
276  Q=M
280  IF TYP(1)=3 THEN 400
290  READ #1;A$,N,D,G,H,J,F
295  READ #2,Q
300  PRINT #2;A$,N,D,G,H,J,F
310  FOR I=1 TO 3*N
320  READ #1;X[I]
330  NEXT I
340  FOR I=1 TO 3*N
350  PRINT #2;X[I]
360  NEXT I
365  M=M+1
370  GOTO 280
380  PRINT C$" IS NOT ON FILE TG2"
390  GOTO 60
400  PRINT C$" HAS BEEN PURGED"
401  READ #1,M
402  PRINT #1,M; END
410  GOTO 60
420  PRINT "UNAUTHORIZED USE OF TGPURG"
430  PRINT "WARNING ONLY"
440  GOTO 450
450  END
```

TGRSTO

```
10  REM PROGRAM TO RESTORE DATA FROM TG2 OR T BACK TO FILE TG
11  PRINT "NAME FILE WHERE DATA IS";
12  INPUT C$
13  ASSIGN C$,1,RO
20  FILES *,TG
30  DIM X[100]
40  DIM A$[72],B$[72],C$[72]
50  PRINT "NAME OF DATA SET TO BE TRANSFERED?"
60  INPUT A$
70  IF A$="0" THEN 280
80  READ #1,1
90  GOTO TYP(1) OF 100,120,150
100  READ #1;X
110  GOTO 90
120  READ #1;B$
130  IF A$=B$ THEN 170
140  GOTO 90
150  PRINT A$"IS NOT ON FILE"C$
155  GOTO 50
160  GOTO 90
170  READ #2,1
171  PRINT #2;B$
172  GOTO TYP(1) OF 180,260,260
180  READ #1;A
181  PRINT #2;A
182  GOTO 172
260  PRINT "DATA FOR "A$" IS NOW IN FILE TG"
261  PRINT #2; END
265  CHAIN "PROXY"
270  STOP
280  END
```